

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-96-1-0227

R&T Code 96PR01987-00

*Tert*-Butyl Alumoxanes: Synthetic Analogs for Methyl Alumoxane (MAO) and New Catalytic  
Routes to Polyolefins and Polyketones

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OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR01987-00  
Contract/Grant Number: N00014-96-1-0227  
Contract/Grant Title: Tert-Butyl Alumoxanes: Synthetic Analogs for Methyl Alumoxane (MAO)  
Principal Investigator: Andrew R. Barron and New Catalytic Routes to Polyolefins and  
Mailing Address: 6100 Main St., MS-60 Polyketones  
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- a. Number of papers submitted to refereed journals, but not published: 10 (see attached)  
b. + Number of papers published in refereed journals (for each, provide a complete citation): 9 (see attached)  
c. + Number of books or chapters submitted, but not yet published: 0  
d. + Number of books or chapters published (for each, provide a complete citation): 0  
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0  
f. Number of patents filed: 0  
g. + Number of patents granted (for each, provide a complete citation): 0  
h. + Number of invited presentations (for each, provide a complete citation): 5 (see attached)  
I. + Number of submitted presentations (for each, provide a complete citation): 2 (see attached)  
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 3 (see attached)

(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions.

Faculty Awards/Offices, etc.)

- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 5

Graduate Students: 2

Post-Doctoral Associates: 3

including the number of,

Female Graduate Students: 1

Female Post-Doctoral Associates: 1

Minority\* Graduate Students: 1

Minority\* Post-Doctoral Associates: 0

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 1

- l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

See attached.

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published.

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

a. Submitted Papers

1. A chemical approach for structural, composite, and coating materials for automotive applications, A. R. Barron, submitted for publication.
2. Carboxylate Substituted Alumoxanes as Processable Precursors to Transition Metal-Aluminum and Lanthanide-Aluminum Mixed Metal Oxides: Atomic Scale Mixing via a New Transmetalation Reaction. A. Kareiva, C. J. Harlan, D. B. MacQueen, R. Cook, and A. R. Barron, *Chem. Mater.*, in press.
3. Stereoregular polymerization of (R,S)-propylene oxide by an alumoxane-propylene oxide complex. B. Wu, C. J. Harlan, R. W. Lenz, and A. R. Barron, *Macromolecules*, in press.
4. Methyl-hydride metathesis between  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}_2$  and  $[(\text{H})\text{Al}(\mu_3\text{-N}^t\text{Bu})]_4$ : molecular structures of  $[\text{Al}(\text{H})_x(\text{Me})_{1-x}(\mu_3\text{-NBu})_4]$  ( $x = 0, 0.78, 1$ ) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{Me})(\mu\text{-H})]_2$ . C. J. Harlan, S. G. Bott, and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
5. Yttrium substituted alumoxanes: a *chemie duce* route to YAG. C. J. Harlan, A. Kareiva, D. B. MacQueen, R. Cook, and A. R. Barron, *Adv. Mater.*, submitted for publication.
6. Structural characterization of dialkylaluminum carboxylates: models for carboxylate alumoxanes, C. E. Bethley, C. L. Aitken, Y. Koide, C. J. Harlan, S. G. Bott, and A. R. Barron, *Organometallics*, submitted for publication.
7. Tert-amyl compounds of aluminum and gallium: halides, hydroxides and chalcogenides. C. J. Harlan, E. G. Gillan, S. G. Bott, and A. R. Barron, *Organometallics*, submitted for publication.
8. Molecular structure of  $[(^t\text{Bu})_2\text{Al}(\mu\text{-NH}^t\text{Bu})]_2$ . S. G. Bott, Y. Koide, and A. R. Barron, *J. Chem. Cryst.*, in press.
9. Reaction of amines with  $[(^t\text{Bu})\text{Al}(\mu_3\text{-O})]_6$ : determination of the steric limitation of a latent Lewis acid. Y. Koide, S. G. Bott, and A. R. Barron, *Organometallics*, submitted for publication.
10. Reaction of group 13-sulfido cubanes with dimethylzirconocene. C. J. Harlan and A. R. Barron, *J. Cluster Chem.*, in press.

b. Published Papers in Refereed Journals

1. Alumoxanes as co-catalysts in palladium catalyzed co-polymerization of carbon monoxide and ethylene: genesis of a structure activity relationship. Y. Koide, S. G. Bott, and A. R. Barron, *Organometallics*, 1996, **15**, 2213.
2. Polyketone polymers prepared using a palladium/alumoxane catalyst system. Y. Koide and A. R. Barron, *Macromolecular*, 1996, **29**, 1110.
3. Reaction of tert-butylalumoxane with ketones. Y. Koide and A. R. Barron, *Main Group Metal. Chem.*, 1995, **18**, 405.
4. Chemical synthesis of poly- $\beta$ -hydroxybutyrate by the polymerization of [R,S]- $\beta$ -butyrolactone with alumoxane catalysts. R. W. Lenz, J. Yang, B. Wu, C. J. Harlan, and A. R. Barron, *Can. J. Microbiology*, 1995, **41**, 274.
5. A new understanding of the co-catalytic activity of alumoxanes: the opening of a black box. A. R. Barron, *Macromol. Symp.*, 1995, **97**, 15.
6.  $[\text{Al}_5(^t\text{Bu})_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_3(\mu\text{-OH})_2(\mu\text{-O}_2\text{CPh})_2]$ : A model for the interaction of carboxylic acids with boehmite. Y. Koide and A. R. Barron, *Organometallics*, 1995, **14**, 4026.
7. The Al-O bond interaction in four-coordinate aluminum aryloxide compounds. A. R. Barron, *Polyhedron*, 1995, **14**, 3197.
8. Crystal structure of  $\text{Al}(^t\text{Bu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ : a molecular "slinky", C. L. Aitken and A. R. Barron, *J. Chem. Cryst.*, 1996, **26**, 297.
9. Molecular structure of  $[(^t\text{Bu})_2\text{Al}(\mu\text{-OPh})]_2$ . C. L. Aitken and A. R. Barron, *J. Chem. Cryst.*, 1996, **26**, 293.

h. Invited Presentations.

1. "Alumoxanes: Destroying a Myth", California Catalysis Conference, University of California, Santa Barbara, CA, Fall 1995.
2. University of Delaware.
3. DuPont Central Research Center.
4. University of North Texas.
5. Washington University.

i. Submitted Presentations

1. "Group 13 Compounds with intramolecular stabilization: New latent Lewis acid catalysts" C. N. McMahon and A. R. Barron, ACS meeting, New Orleans, LA, Spring 1996.
2. "Carboxylate compounds of Aluminum", Charles Bethley, S. G. Bott, and A. R. Barron, ACS meeting, New Orleans, LA, Spring 1996.

j. Honors/Awards/Prizes

1. Corday-Morgan Medal and Prize, Royal Society of Chemistry.
2. Editorial Board, *Advanced Materials*.
3. Editorial Board, *Main Group Metals Chemistry*.

1. Other funding: 6/1/93 - 5/31/96.

1. ONR "Gallium and Indium Chalcogenides: Molecules, New Phases and Applications", \$169,593.
2. ONR/STTR "Highly Processable Pre-ceramic Polymers", \$ 39,875.
3. Welch Foundation "New High Latent Lewis Acidic Catalysts", \$ 102,000.
4. NSF travel award "Gas phase structures of MOCVD Precursors to Group 13 Materials", \$ 18,000.

## PHYSICAL S&T DIVISION REPORT PART II

a. Andrew R. Barron

b. 713 737 5610

c. Kenneth Wynne

### d. Program Objectives.

Alumoxanes are the products from the partial hydrolysis of aluminum compounds. While they have been known for over 30 years, and as a class of chemical are highly important industrially, there has been almost no basic understanding of their structure, reactivity, or potential as new inorganic polymers. The aim of this research was to gain a fundamental understanding of alumoxanes and to enable multiple practical applications to be generated from such understanding. Three areas were originally targeted: (1) alumoxanes as ceramic precursors, (2) alkylalumoxanes as polymerization catalysts, and (3) alumoxanes as materials in their own right. Significant advances have been made in the first two areas. We demonstrated that alumoxanes formed from the hydrolysis of aluminum compounds during ceramic synthesis are not linear polymers as previously depicted, but nano-sized "molecules" consisting of a boehmite-like core and an organic periphery. This allowed for the rational synthesis of alumoxanes from a commercially viable starting material, boehmite  $[\text{Al}(\text{O})(\text{OH})]$ . We have previously crystallographically characterized alkylalumoxanes and shown that the active catalysts are cages whose activity is dependent on their "latent Lewis acidity". Future research is primarily directed towards the application of alumoxanes as materials for new  $\text{Li}^+$  and  $\text{H}^+$  electrolytes for battery and fuel cell applications, photochromic materials, polymer lasers, and NLO materials.

### e. Significant results during the last year.

#### **Alumoxanes as ceramic precursors** - Recent results include:

1. The discovery that transition metal and lanthanide cations are readily incorporated into the alumoxane structure provides a simple route to almost any aluminum-based oxide ceramic.
2. The creation of the first aqueous, non-acid, non-hydrocarbon (environmentally benign) process for aluminum based ceramics.
3. The theoretical and structural demonstration as to why carboxylic acids are the ideal ligand for alumoxanes.

The impact of these results include: the ability to limit environmental pollution (and reduce costs) in the processing alumina (and related materials), and the low cost generation of mixed metal oxides without the inherent difficulties of sol-gel type processing.

#### **Alkylalumoxanes as polymerization catalysts** - Recent results and impact include:

1. Development of a Pd-alumoxane catalyst for the co-polymerization of CO and olefins, and its use for the synthesis of very high density high molecular weight polyketone.
2. Design of a method for measuring an alumoxanes "latent Lewis acidity", i.e., its potential activity as a catalyst.
3. Conceptualization of the association between transition metal-alumoxane catalyst systems and biological enzyme systems.
4. Application of our new alkylalumoxanes as catalysts for the polymerization of  $[\text{R},\text{S}]\text{-}\beta\text{-butyrolactone}$  and  $(\text{R},\text{S})\text{-propylene oxide}$ .

5. Investigation of model compounds to understand the mode of catalytic activity of alumoxanes

The impact of these results include: Several companies (Albemarle, Hoechst, and Idemitsu) are presently applying our results to enhance catalyst activity and develop new catalysts.

f. Next years work.

The design of organic molecules with desirable physical properties has long been understood. Unfortunately, they are often too unstable to consider for long-term applications in severe environments or high temperatures. In contrast, ceramics have the physical properties that make them durable, but the *design* of controllable physical properties is in its infancy. Attempts have been made to prepare hybrid inorganic/organic materials that can offer designed optical properties with physical strength and resilience. We propose that the alumoxanes have the ability to offer high stability with processability in a number of optical and electronic applications. We propose to investigate the feasibility of this approach in the following areas:

1. Lithium and  $H^+$  ion doped polyether alumoxanes will be investigated as highly stable polymer electrolytes in lithium/polymer batteries and fuel cells, respectively.
2. Doped-alumoxanes offer a new technology for photochromic materials.
3. Alumoxanes make ideal matrix materials (both active and passive) for organic laser dyes with large cross-sections for absorption, lower threshold power, and the ability to tune the frequency response.
4. Alumoxanes have suitable properties as a new NLO materials for data storage applications.
5. The chemical (and thermal) cross-linking provides an ideal manner for near net shape processing, injection molding and direct write-type processes.

- g. Julie Francis - graduate student  
Charles Bethley - graduate student  
Dr. C. Jeff Harlan - post doctoral fellow  
Dr. Yoshihiro Koide - post-doctoral fellow

## PHYSICAL S&T DIVISION REPORT

### PART III

#### c. Explanatory text.

(a) Alumoxanes are aluminum-oxygen macromolecules. They are formed from the partial hydrolysis of aluminum compounds. They are often given the general formula of  $[(X)Al(O)]_n$ . There is a wide range of commercial applications for alumoxanes at the present, including: (1) If X is an alkyl group (i.e., methyl, ethyl etc.) then alumoxanes are used as catalysts for polyolefins, polyethers, and polyester synthesis, (2) Traditionally, sol-gels used for aluminum-based ceramics synthesis are in fact alkoxide or carboxylate alumoxanes, (3) Carboxylate alumoxanes are also used in paints and printing ink, in wood treatment, damp proofing and masonry, in the textiles industry, and as additives in lubricating oils and greases. (4) Chloro-alumoxanes are the most common anti-perspirants. Despite these applications nothing was known of their structure or physical properties, and there was no understanding of their chemical reactions.

We have systematically studied the structure and reactivity of alumoxanes. In addition, to the direct application of the results to the areas of ceramic processing and homogeneous catalysis, we have been able to develop the alumoxane as a material in its own right. We can alter the chemical and physical properties easily, and have developed environmentally benign syntheses and processes for a wide range of applications.

[Visual aid] An important development has been the direct replacement of a transition metal or lanthanide into the alumoxane structure, at room temperature, in aqueous solution, to allow for a divers range of materials to be prepared using a single basic reagent.

(b) Alumoxanes as catalysts - An understanding that the activity of alumoxanes is due to their "latent Lewis acidity" (i.e., the ability of the cage to open creating a highly active site) has allowed us to develop several new designed catalyst systems. The co-polymerization of carbon monoxide and ethylene is typically accomplished by a cationic palladium catalyst in the presence of an acid derived counter-ion. However, the acid causes the premature decomposition of the polyketone polymer. In contrast, use of an alumoxane co-catalyst allows for polyketone polymers of unusually high density and thermal stability to be prepared.

(c) Alumoxanes as Ceramic precursors - The novel transmetalation reaction between  $M(acac)_n$  ( $M$  = alkali, alkali earth, transition metal or lanthanide) and carboxylate alumoxanes,  $[Al(O)_x(OH)_y(O_2CR)_z]_n$ , yields the doped alumoxane which is a highly processable precursor to the appropriate ceramic. This provides the advantages of sol-gel methods without any of the disadvantages, at a price and simplicity that is comparable to traditional ceramic processing. A comparison of the advantages and disadvantages is given in the table.

# Alumoxanes: Catalysts, Ceramic Precursors and Materials

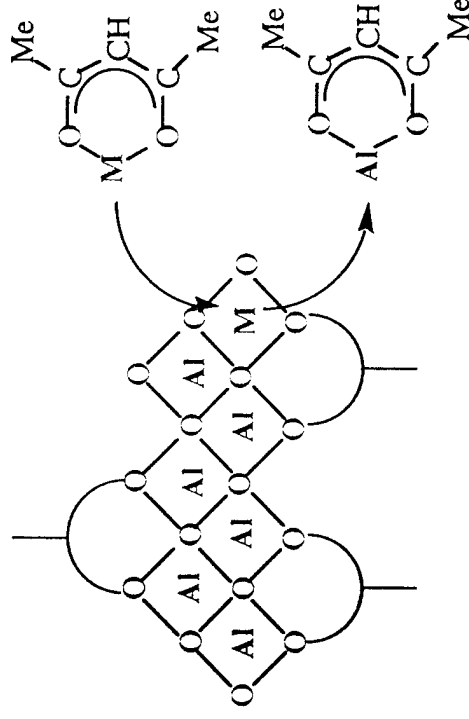
Andrew R. Barron, Rice University

## Objectives:

- . Determine the structure(s), reactivity, and physical properties of alumoxanes.

## Challenges:

- . Alumoxanes have been studied for over 30 years.
- . No prior understanding of reactions.
- . Complex mixture of multiple species.



## Approach:

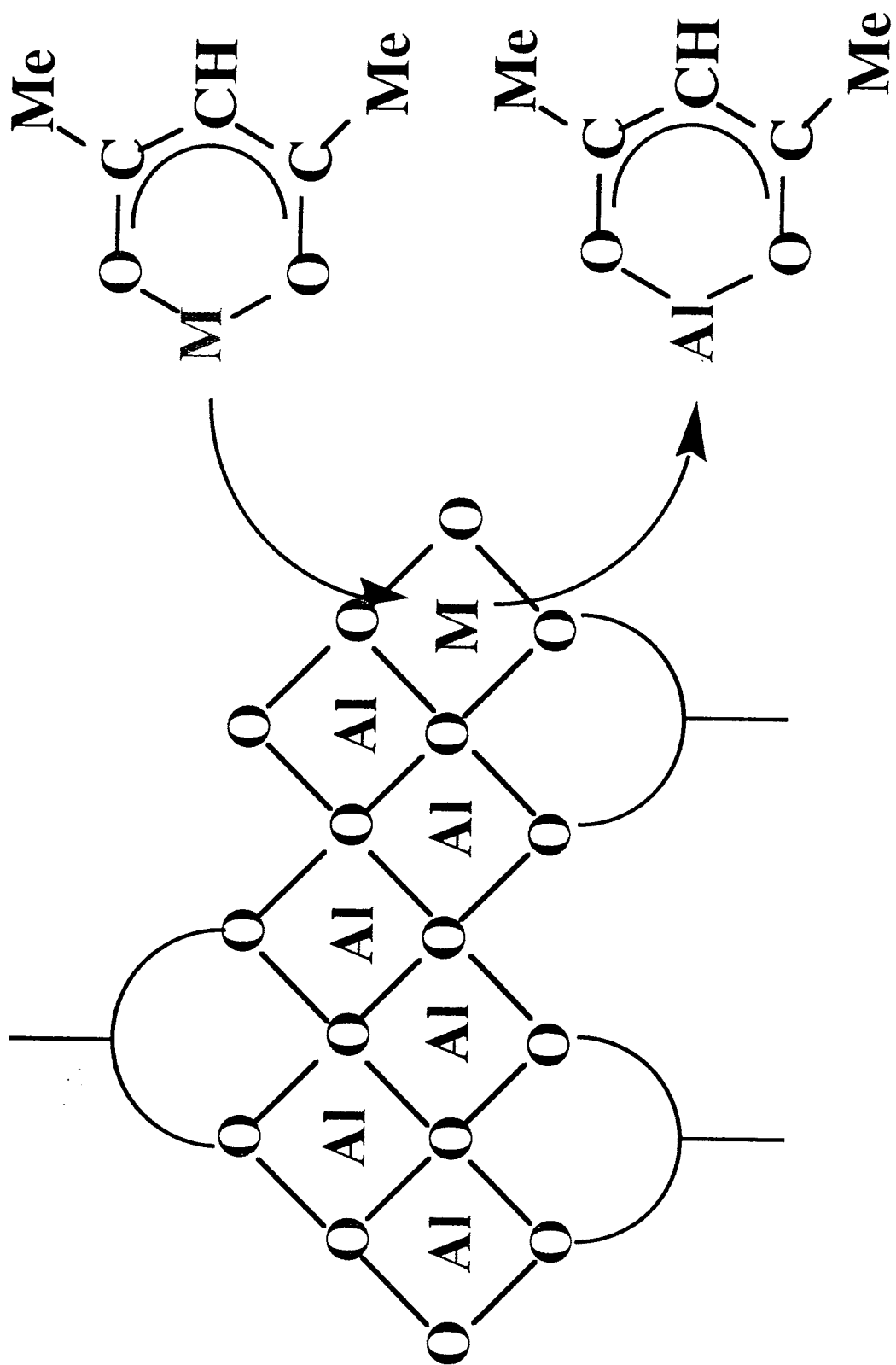
- . Structural characterization using diverse methods.
- . Synthesis and structural evaluation of model compounds.
- . Design new economic and environmentally benign syntheses based upon structural results.
- . Investigate direct "real world" application as new materials.

## Accomplishments:

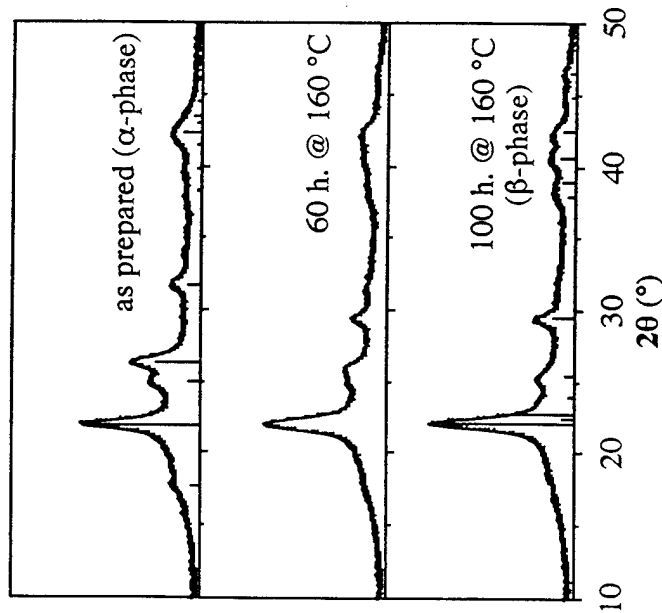
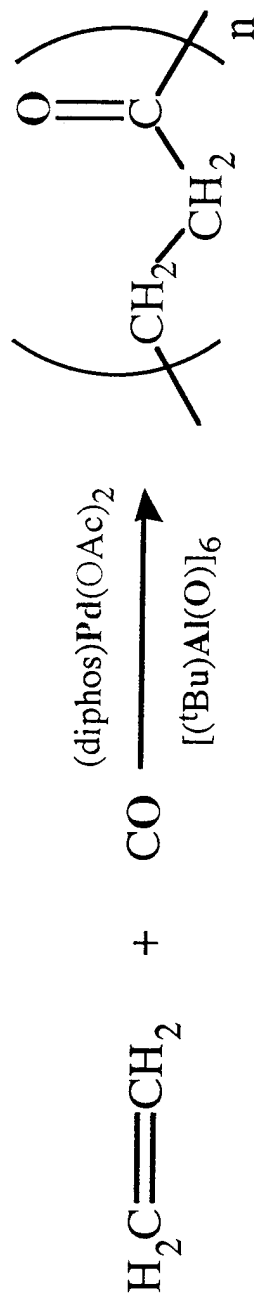
- . Full structural characterization of alumoxanes.
- . New model for catalytic activity proposed - latent Lewis acidity
- . New rational synthesis of alumoxanes from boehmite.
- . Room temperature route to mixed metal alumoxanes.
- . First all aqueous processing of alumina-based ceramics.

## Transitions:

- . Patents being filed by Rice.
- . Licensing agreement w. TDA for ceramic synthesis.
- . Development agreement with Gentex, for application as scratch resistant coatings for polycarbonate.
- . Sponsored research with Albemarle, Hoechst, and Idemitsu for olefin polymerization catalyst.



# Polyketone Polymers Prepared Using a Pd/Alumoxane Catalyst System



XRD of Pd/alumoxane polyketone, demonstrating the high thermal stability.

Crystal Data for Polyketones: Literature versus Pd/Alumoxane

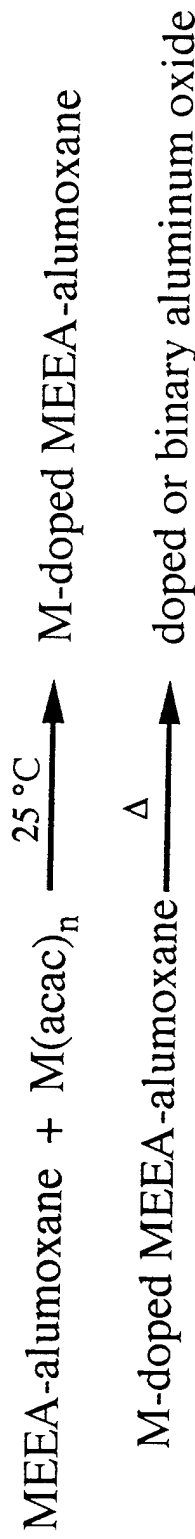
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	<i>d</i> <sub>calc</sub> (g.cm <sup>-3</sup> )
Pd/alumoxane	6.79	5.02	7.55	257.3	1.445
Pd/acid system	6.91	5.12	7.60	268.8	1.383

Catalysis: *Organometallics*, 1996, **15**, 2213

Polymer: *Macromolecules*, 1996, **29**, 1110

# Alumoxane Synthesis of Aluminum Based Ceramics

General reaction (MEEA-H = methoxy(ethoxyethoxy)acetic acid



## Comparison of the alumoxane method with the ceramic method and sol-gel syntheses

	Alumoxane	Sol-gel	Ceramic
methodology	simple	complex	simple
atomic scale mixing	yes	yes	no
meta-stable phases	yes	yes	no
stability	excellent	poor	infinite
solubility	readily controlled	difficult to control	none
processability	good	good	poor
time	< 8 h.	> 20 h.	days
cost	low	med. - high	low